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SILVER(I) COORDINATION COMPOUNDS WITH POLYDENTATE PYRIMIDINE LIGANDS: THERMOCHROMISM OF LUMINESCENCE*

Keywords: polydentate pyrimidine ligands, silver(I), white luminescence, thermochromic behavior.

Designing luminescent coordination compounds is of current interest in modern coordination chemistry due to applications of these compounds in organic light emitting diodes (OLEDs) [1–2]. Synthesis and investigation of luminescent silver(I) complexes is a specially prospective task since many Ag(I) complexes exhibit bright fluorescence or phosphorescence in visible spectral region [3–4]. In the current work we use pyrimidine-based ligands to synthesize Ag(I) complexes (fig. 1). The ligands, Ln, with various *N*-heterocycles in the position 2 of the pyrimidine ring can adopt various coordination modes. Furthermore, these ligands differ by their electronic properties (π-donor or π-acceptor) and can significantly influence on the stability and emission properties of the complexes.

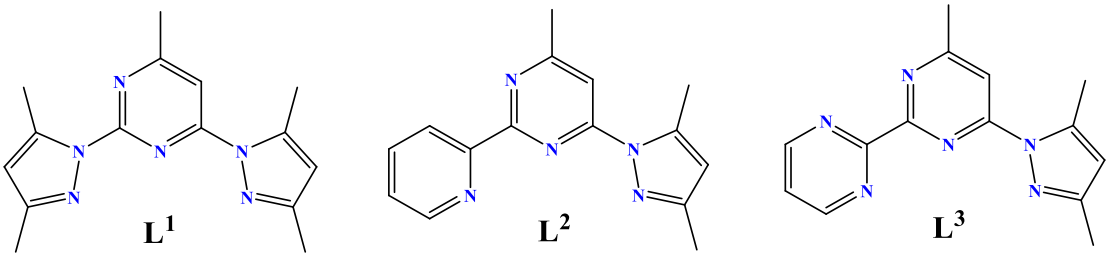

Figure 1. Polydentate pyrimidine-based ligands

The main goal of this work is to study how the substituent in position 2 of the pyrimidine ring affects both luminescent properties and structures of silver(I) complexes. A series of coordination compounds, $[AgL^1NO_3]$, $[AgL^1X]_n$, $[Ag_2(L^2)_2X_2]$

($X = I^-$, Br^-, Cl^-), $[AgL^1(PPh_3)Y]$ ($Y = CF_3SO_3^-$, BF_4^-, NO_3^-), $[AgL^3NO_3 \cdot CH_3CN]_n$, have been synthesized and structurally characterized. According to the X-ray single data, the complexes $[AgL^1NO_3]$, $[AgL^1(PPh_3)Y]$ adopt mononuclear structures; the complexes $[Ag_2(L^2)_2X_2]$ are binuclear; $[AgL^1X]_n$ and $[AgL^3NO_3 \cdot CH_3CN]_n$ are polymeric compounds (fig. 2).

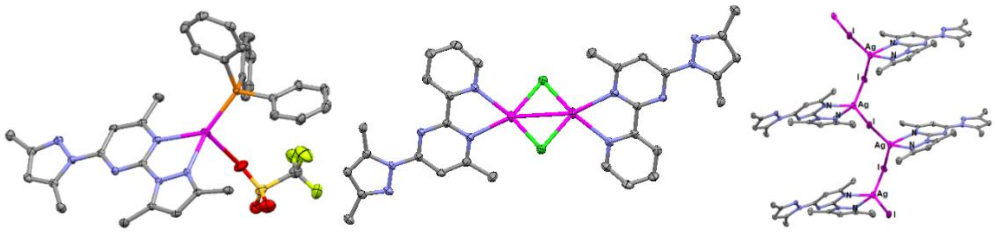

Figure 2. Crystal structures of the complexes $[AgL^1(PPh_3)CF_3SO_3]$ (left), $[Ag_2(L^2)_2Cl_2]$ (middle), $[AgL^1I]_n$ (right)

The emission spectrum maximum of $[Ag_2(L^2)_2I_2]$ is at 576 nm (yellow luminescence) and it is not excitation wavelength dependent. The complex $[AgL^3NO_3 \cdot CH_3CN]_n$ does not show luminescence at room temperature. The complexes $[AgL^1(PPh_3)Y]$ have similar photoluminescent properties – the emission bands are wide with maxima at 400-500 nm (white luminescence). The complex $[AgL^1(PPh_3)CF_3SO_3]$ shows temperature and excitation wavelength dependent phosphorescence (Fig. 3). There is a bathochromic shift of the emission band upon decrease of temperature from 300 K to 77 K.

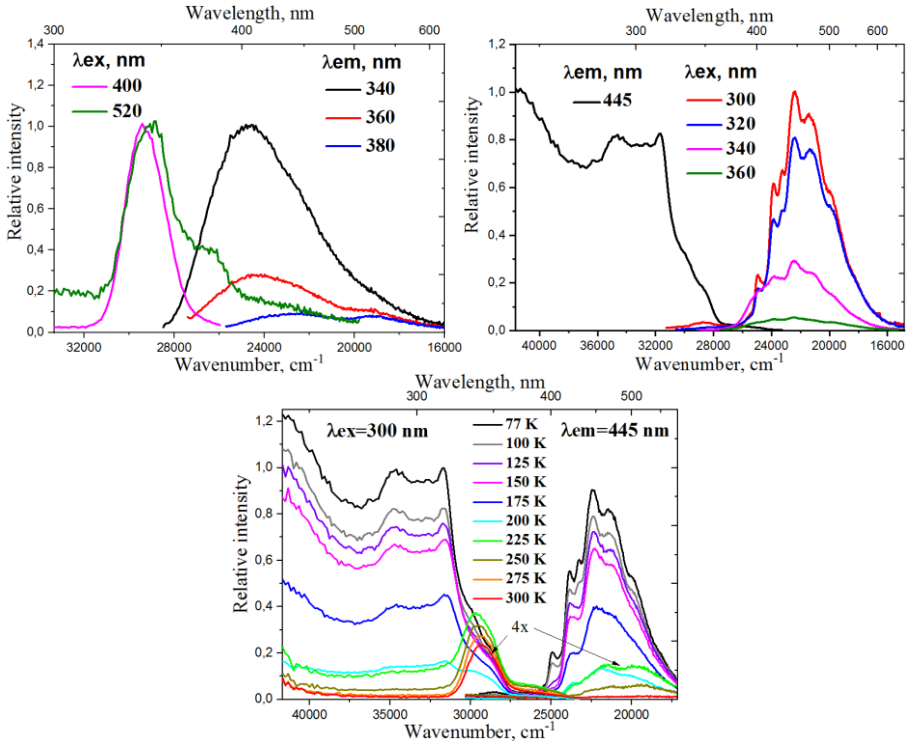

Figure 3. Photoluminescence of $[AgL^1(PPh_3)CF_3SO_3]$ at different excitations at 300 K (left); at different excitations at 77 K (middle); at different temperatures at λ_{ex} = 300 nm and λ_{em} = 445 nm (right)

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TIME-DEPENDENT DENSITY FUNCTIONAL THEORY STUDY OF THE LUMINESCENCE OF 2-AMINOPYRIMIDINE DERIVATIVE

Keywords: fluorescence, pyrimidine, TD-DFT calculations, excited state double proton transfer, excitation wavelength dependent emission.

The excitation wavelength dependent photoluminescence property has aroused great research interest due to its potential applications in sensors, optoelectronic devices, biological labelling and information encryption [1–3]. Dual fluorescence behavior in the solid state depending on excitation energy is typical for pyridine and pyrimidine derivatives [4–5]. High-energy emission band is ascribed to the fluorescence of a monomeric molecule while low-energy emission band is related to the fluorescence of a tautomeric dimeric associate formed as a result of excited state double proton transfer (ESDPT) process (fig. 1). In the last case two protons are shifted from the amino groups to aza-atoms of the pyrimidine ring in the $\{N–H\cdots N\}_2$ hydrogen bonding synthon.

Recently our group reported dual excitation wavelength dependent fluorescence in 2-amino-4-methylpyrimidine (L, fig. 1) [6]. To gain insight into the phenomenon of